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**Vinyl Polymerization by Metal Complexes. VII.*
Photopolymerization of Vinyl Monomers by
Metal Salt-Saccharide Systems**

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ABSTRACT

The photopolymerization of vinyl monomers by metal salt-saccharide system was investigated in various solvents. The rate of polymerization in the presence of an iron(III) salt in aqueous media was remarkably accelerated by the addition of saccharides. The acceleration caused by a series of saccharides was found to be in the following order: glucose > fructose > lactose = maltose. α -Methyl-d-glucoside and sucrose exhibited very little effect. The overall activation energy for the photopolymerization of acrylonitrile in the presence of glucose was found to be 2.7 kcal/mole, about half of the value obtained in the absence of glucose.

*For Part VI of this series, see K. Azuma, Y. Inaki, and K. Takemoto, Makromol. Chem., **166**, 189 (1973).

INTRODUCTION

In previous papers of this series, the polymerization of vinyl monomers by copper complexes with oligo(*n*)ethylene-(*n* + 1)amine, nylon 6, and its oligomers have been reported [1-6]. In these systems it was suggested that the interaction between metal ion and N-ligand was significant for initiating polymerization.

In the course of successive investigations, we found that the polymerization of acrylonitrile by iron (III) nitrate in aqueous media was remarkably accelerated by the addition of glucose in diffuse light. In this system the interaction between metal ion and O-ligands seems to be substantial and such a reaction is interesting with respect to the problem of biochemical free radical formation in nature. The present paper considers the photopolymerization of vinyl monomers by metal ion-saccharide systems in various solvents, and the initiation mechanism is discussed.

EXPERIMENTAL

Materials

Acrylonitrile, methyl methacrylate, and styrene were purified by distillation under reduced pressure. Solvents used were purified by the usual methods. Both the metal salts and saccharides used were of commercial origin.

Polymerization

Photopolymerization was carried out in a sealed tube of hard glass of 1.8 cm diameter. The light source employed a high-pressure mercury vapor lamp (Toshiba SH-100UV-2) in a hard glass envelope. The sealed tubes were rotated around the lamp at a distance of 10 cm. Vinyl monomer, metal salt, and saccharide solution were charged into a tube in the dark. The degassed and sealed tube was then irradiated in an ice-cold water bath at 0°C. The polymer was obtained as colorless precipitates by pouring the contents into a large excess of methanol and drying overnight under vacuum.

Molecular Weight of Polymer

The intrinsic viscosity of polyacrylonitrile was measured in dimethylformamide solution at 25°C. The molecular weight of the polymer was calculated according to

$$[\eta] = 2.43 \times 10^{-4} M^{0.73} \quad [7]$$

RESULTS AND DISCUSSION

Preliminary Polymerization

Thermal polymerization of acrylonitrile by iron(III) nitrate-saccharide systems was carried out in aqueous media in the dark at 60°C for 5 hr (Table 1). In the absence of saccharide, only a small amount of polymerization of acrylonitrile by iron(III) nitrate was observed. The iron(III)-saccharide system, however, could initiate the polymerization of acrylonitrile, especially in the case of fructose.

Iron(III) salts are known to serve generally as inhibitors for the polymerization of vinyl monomers. On the other hand, vinyl polymerization by iron(III) salt was reported in a few papers, such as the polymerization of acrylamide by iron(III) nitrate [8]. In our case the carbonyl group of the fructose might be related to the initiation process.

Photopolymerization

Photopolymerization of acrylonitrile with iron(III)-saccharide systems was carried out in aqueous media at 0°C. The results are shown in Table 2. A comparison of Tables 1 and 2 reveals that the rate of photopolymerization at 0°C was much greater than that of thermal polymerization at 60°C.

TABLE 1. Thermal Polymerization of AN with Various Ferric Salt-Saccharide Systems^a

Saccharide	Mole/liter	Yield (%)
None	-	0.4
Glucose	0.111	1.1
α -Methyl-d-glucoside	0.103	0.6
Fructose	0.111	9.8
Lactose	0.056	1.2
Maltose	0.056	1.7
Sucrose	0.056	2.1

^a[Fe(NO₃)₃·9H₂O] = 5.0 × 10⁻³ mole/liter, [AN] = 1.01 mole/liter, 60°C, 5 hr, in H₂O.

TABLE 2. Photopolymerization of AN with Various Ferric Nitrate-Saccharide Systems^a

Saccharide	Mole/liter	Yield (%)	M × 10 ⁻⁵
None	-	6.0	2.51
Glucose	0.111	36.7 ^b	1.71
α-Methyl-d-glucoside	0.103	6.4	2.57
Fructose	0.111	29.8	1.38
Lactose	0.056	23.8	1.95
Maltose	0.056	23.3	1.75
Sucrose	0.056	5.2	2.60

^a[Fe(NO₃)₃·9H₂O] = 5.0 × 10⁻³ mole/liter, [AN] = 1.01 mole/liter, 0°C, 20 min, in H₂O.

^bThe yield was 26.7% when 0.056 mole/liter of glucose was present.

The addition of saccharide remarkably increased the rate of photopolymerization of acrylonitrile as shown in Table 2. The order of acceleration by the addition of saccharides was found to be as follows: glucose > fructose > lactose = maltose. α-Methyl-d-glucoside and sucrose showed little effect on the photopolymerization of acrylonitrile.

The acceleration caused by saccharide might be attributed to the interaction and/or chelate formation of functional groups of saccharide, such as -OH, -CO, and -CHO, with iron(III) ion. As compared with the case of adding saccharide (0.056 mole/liter in Table 2), glucose, lactose, and maltose, which are aldoses having the -CHO group, showed almost the same activity for the photopolymerization of acrylonitrile with iron(III) nitrate. Fructose, which is a ketose having -C=O groups, also gave an activity similar to the three saccharides mentioned here for the photopolymerization of acrylonitrile. However, because the other saccharides have no reducing end groups, such as α-methyl-d-glucoside and sucrose, the photopolymerization of acrylonitrile was affected very little. These facts suggest that the reducing end group of saccharide seems to be significant for the photopolymerization of acrylonitrile with iron(III) nitrate.

Photopolymerization with Various Metal Salts

The photopolymerization of acrylonitrile with a variety of metal salt-saccharide systems was investigated in aqueous media at 0°C.

TABLE 3. Photopolymerization of AN with Various Metal Salts^a

Salt	Glucose (mole/liter)	Time (min)	Yield (%)
FeCl ₃ ·6H ₂ O	0.000	20	7.0
	0.111	20	23.8
Fe(NO ₃) ₃ ·9H ₂ O	0.000	20	6.0
	0.111	20	36.7
Al(NO ₃) ₃ ·9H ₂ O	0.000	390	3.6
	0.111	390	3.3
Co(NO ₃) ₂ ·6H ₂ O	0.000	390	1.8
	0.111	390	1.1
	0.111	390	1.1
Ni(NO ₃) ₂ ·6H ₂ O	0.000	390	2.4
	0.111	390	1.9
Cu(NO ₃) ₂ ·H ₂ O	0.000	390	1.2
	0.111	390	1.9

^a[Metal salt] = 5.0×10^{-3} mole/liter, [AN] = 1.01 mole/liter, 0°C, in H₂O.

The results of the photopolymerization are shown in Table 3. Iron(III) salts, particularly in the presence of glucose, showed the highest activity for initiating the photopolymerization of acrylonitrile. Other metals such as Cu(II), Co(II), Ni(II), and Mg(II) were found to be less active, even in the presence of glucose. In general, metal chlorides other than iron(III) could not initiate the photopolymerization of acrylonitrile. Little difference in the initiation activity was found for iron(III) salts between nitrate and chloride for the photopolymerization of acrylonitrile. This difference might be attributed to the strength of the gegen anions coordinated to the metal ion.

Photopolymerization of Vinyl Monomers in Various Solvents

The photopolymerization of acrylonitrile, methyl methacrylate, and styrene initiated with iron(III) chloride-saccharide system was carried out in aprotic solvents at 0°C. Dimethylformamide, pyridine, and

TABLE 4. Photopolymerization of Vinyl Monomers in DMF and PD at 0°C, and in DMSO^a

Monomer	Solvent	Glucose (mole/liter)	Time (min)	Yield (%)
AN	DMF	0.000	90	4.4
		0.111	90	4.9
	PD	0.000	180	4.1
		0.055	180	8.9
	DMSO	0.000	180	13.3
		0.111	180	14.5
MMA	DMF	0.000	90	1.2
		0.111	90	1.6
	PD	0.000	180	1.1
		0.056	180	1.7
	DMSO	0.000	180	13.3
		0.111	180	16.1

^aDMF, dimethylformamide; PD, pyridine; and DMSO, dimethylsulfoxide. $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}] = 5.0 \times 10^{-3}$ mole/liter, monomer = 2 ml, solvent = 8 ml, 10°C.

dimethylsulfoxide were used as solvents for the polymerization. The results of the photopolymerization of acrylonitrile and methyl methacrylate are tabulated in Table 4. The polymerization of styrene could not be initiated by these systems, while a relatively high conversion was attained for acrylonitrile and methyl methacrylate.

Rates of a photopolymerization in aprotic solvents were generally slow compared with that observed in aqueous media. Relatively high conversion was obtained in DMSO. The addition of glucose scarcely accelerated photopolymerization in these aprotic solvents. This might be attributed to the difference in coordination abilities of glucose and solvent. A dark brown discoloration in the case of the iron(III)-aprotic solvent system might indicate the formation of the solvated iron(III) ion.

Effect of Temperature on Photopolymerization

Photopolymerization of acrylonitrile with iron(III)-glucose system at 0-30°C was carried out in aqueous media. Arrhenius plots from

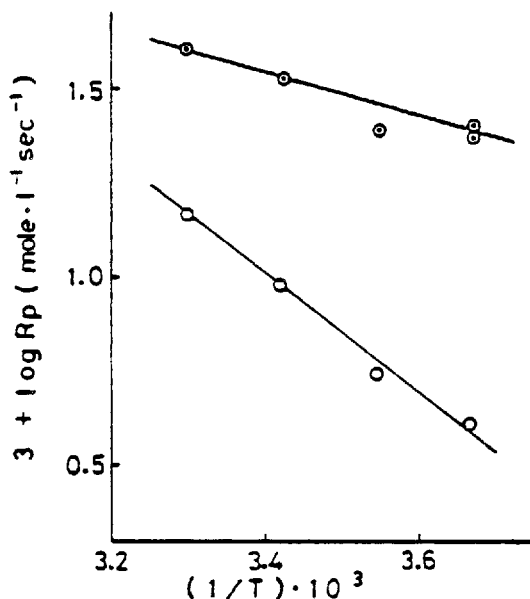


FIG. 1. Arrhenius plots for the photopolymerization of acrylonitrile in aqueous media: ○ in the presence of iron(III) nitrate, and ⊙ in the presence of iron(III) nitrate-glucose system.

these photopolymerizations gave a straight line as shown in Fig. 1. The overall activation energy for the photopolymerization was estimated from the slope of the line in Fig. 1 as follows:

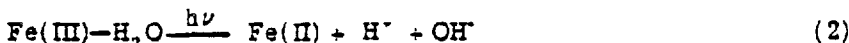
iron(III) nitrate: 5.8 kcal/mole

iron(III) nitrate-glucose: 2.7 kcal/mole

It is to be noted that the value of the case initiated by the iron(III)-glucose system was found to be lower than that of the case initiated by iron(III) nitrate.

Initiation Mechanism

The initiation mechanism for the photopolymerization with iron(III) ion in aqueous solution has been proposed by Dainton and Sisley as follows [9]:



As was mentioned above in our cases, the rate of photopolymerization was accelerated by the addition of saccharide. Therefore, it is reasonable to assume that the saccharide-iron(III) complex would participate in the photopolymerization initiation process. Furthermore, reduction of iron(III) to iron(II) during the polymerization process was confirmed spectrophotometrically by using the o-phenanthroline method of Moss et al. [10]. It is relevant to our results that the formation of the gluconic acid-iron(III) complex has been reported by Pecsok and Sandera [11]. From these considerations the initiation mechanism of photopolymerization with the iron(III) salt-saccharide system is proposed to be as follows:



where S-H denotes a saccharide molecule.

In polymerization with the glucose-cerium(IV) system it was assumed that glucose is oxidized and forms a free radical by breaking the C-C bond [12]. A similar mechanism for glucose oxidation could also be applied to our case.

Further kinetic and physicochemical studies on the interaction between iron(III) and saccharide and on the detailed initiation mechanism will be reported in our next paper.

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